PROPERTIES OF COMPOSITE ELECTRODEPOSITS

FINAL REPORT

R. WEIL AND C. SHEU

SEPTEMBER 1, 1990

U. S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAALO3-87-K-0047

STEVENS INSTITUTE OF TECHNOLOGY

DTIC
ELECTE
OCT.26 1990
S
B
D

APPROVED FOR PUBLIC RELEASE;
DITRIBUTION UNLIMITED.

90 10 23 099

THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE
THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL
DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO
DESIGNATED BY OTHER DOCUMENTATION.

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS			
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.			
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 24167.9-MS			
6a. NAME OF PERFORMING ORGANIZATION Stevens Institute of Technology	6b. OFFICE SYMBOL *(If applicable)*	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office			
6c. ADDRESS *(City, State, and ZIP Code)* Castle Point Station Hoboken, NJ 07030		7b. ADDRESS *(City, State, and ZIP Code)* P. O. Box 12211 Research Triangle Park, NC 27709-2211			
8a NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL *(If applicable)*	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-87-K-0047			
8c. ADDRESS *(City, State, and ZIP Code)* P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(include Security Classification)*

Properties of Composite Electrodeposits   Unclassified

12. PERSONAL AUTHOR(S)   R. Weil and C. Sheu

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM July 1987 TO Aug. 1990	14. DATE OF REPORT *(Year, Month, Day)* Sept. 1, 1990	15. PAGE COUNT 17

16 SUPPLEMENTARY NOTATION   The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17	COSATI CODES		18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The corrosion and tribological properties of multilayer, electrodeposited chromium composites were determined. The composites consisted of 250 nm-thick layers of crystalline and amorphous chromium, chromium and its hydride, and alloys of different molybdenum or carbon contents. The properties were compared with those of single-layer deposits of the same materials. The effect of sandwiching a layer of the intermetallic phase, NiSn on the mechanical and corrosion properties of electrodeposited tin and nickel was also investigated. It was found that multilayer chromium deposits of different molybdenum contents exhibited superior corrosion resistance

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE *(Include Area Code)*	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.   UNCLASSIFIED

19.

in sulfuric acid. Multilayer deposits of crystalline and amorphous chromium and of different carbon contents also had better corrosion resistance than the single-layer ones especially in hydrochloric acid. The attack of substrates by the chrome-plating solutions before they become covered by deposits was found to result in redeposition of the dissolved ions to form alloy layers with chromium under certain conditions. The sandwiching of NiSn between nickel layers increased the yield and tensile strengths without adversely affecting the ductility and prevented corrosion pits from reaching a steel substrate. The tribological properties of single and multilayer deposits did not differ significantly.

Accession For	
NTIS GRA&I	☑
DTIC TAB	☐
Unannounced	☐
Justification	

By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

INTRODUCTION

Most of the effort during the period covered by this report; namely, June 1987 to August 1990, was directed towards the investigation of multilayer composites consisting primarily of electrodeposited chromium. This metal was selected because of its importance in many applications of interest to the Army. Also special attention was given to the solutions which contained trivalent ions because they are ecologically preferable. The properties which were attempted to be improved were the resistance to corrosion, friction and wear. Because chromium is inherently brittle, no attempt was made to improve the mechanical properties. The hardness was of interest because of the tribological properties of chromium. The improvement of the mechanical properties, i.e., yield and tensile strength and ductility was investigated in electrodeposited nickel and tin by the inclusion of a layer of the intermetallic compound NiSn. The corrosion resistance of these deposits was also investigated.

One type of chromium-base composite which was investigated consisted of alternate layers of a low and a higher molybdenum content. Another type consisted of alternate layers of crystalline and amorphous chromium. A third type consisted of chromium and chromium hydride. Chromium deposited in a solution containing trivalent ions sometimes exhibits the so-called banded structure characterized by alternate dark and lighter bands observed in metallographically prepared cross sections. The dark bands differ in composition from the lighter ones. These deposits are thus naturally occurring composites and were therefore included in the investigation. Chrome-plating solutions attack most substrates before they are covered with a deposit. Therefore the interaction between the deposit and substrate was also studied. As the internal stresses can cause cracking of the deposit and thereby adversely affect the corrosion resistance, they also had to be determined.

EXPERIMENTAL PROCEDURE

Three types of substrates were used. For the corrosion experiments, 0.075 mm-thick, low-carbon steel was the substrate. It was also used when internal stresses were measured. Prior to plating, the steel substrates were dipped in 10% HCl for 3 minutes and then rinsed in distilled water. Copper foil, which was 0.075 mm thick, also was the substrate for stress measurement. The copper foil was also the substrate when the mechanical properties were to be determined because it could be dissolved in a chromic-sulfuric-acids mixture which does not attack chromium or nickel. The copper foil was electropolished in a 67% phosphoric-acid solution at 1.7 V for 3-5 minutes, rinsed in 15% phosphoric acid to remove insoluble phosphates, dipped into 5% sodium hydroxide and 10% sulfuric acid. It was rinsed in distilled water between the various steps and before plating. The interaction between the substrates and the deposit resulting from the attack by the chrome-plating solution was studied with the steel and copper substrates and also nickel. The nickel substrate was produced by plating this metal from a Watts solution on the electropolished copper foil.

The Cr-Mo deposits were plated in solutions of two different compositions. One solution kept at 60°C contained 300 g/l ammonium molybdate and 2.5 g/l sulfuric acid. When the current density was 2 KA/m^2 (kiloamperes per square

meter), the deposit contained about 0.1% Mo. At 10 KA/m^2 the Mo content was about 1.4%. Multilayer deposits were produced by alternately plating at the two current densities. The plating times were adjusted so that each layer was 250 nm thick for total thicknesses of 2 and 5 μm. Single-layer deposits were also plated at the two current densities to the same total thicknesses for comparison. By increasing the concentration of ammonium molybdate to 100 g/l it was possible to increase the molybdenum content of the deposit to about 2% when the higher current density was used. The molybdenum content remained about 0.1% at the lower current density. Single and multilayer deposits with the higher molybdenum content were also produced.

The crystalline-amorphous multilayer deposits were produced in a solution containing 250 g/l chromic oxide, 5 g/l sulfuric acid and 40 ml/l (milliliters per liter) formic acid at room temperature. When the current density was 1 KA/m^2, the deposit was crystalline. It was amorphous at 10 KA/m^2. Alternate layers 25 g/10 nm thick were plated at the two current densities to a total thickness of 3 μm. Single-layer deposits which were 3 μm thick were also plated at the two current densities for comparison. The amorphous deposits exhibited the banded structure.

Multilayer deposits consisting of body-centered-cubic chromium and the hexagonal chromium hydride were plated in a solution containing 175 g/l chromic oxide, 5 g/l sulfuric acid and 0.5 ml/l formic acid at ambient temperature. When the current density was 3 KA/m^2, deposits were cubic. They were hexagonal at 1 KA/m^2. Single and multilayer deposits were plated to a thickness of 3 μm. The individual layers in the multilayer deposits were again 250 nm thick.

Sandwiches of nickel "bread" and a layer of the metastable intermetallic phase, NiSn and of tin "bread" also with NiSn could not be plated by just varying the plating conditions. Tin was pulse plated in a solution containing 200 ml/l stannous fluoborate, 15 ml/l fluoboric acid, 6 g/l gelatin and 1 g/l beta naphthol. The square-wave, peak current density was 4 A/m^2, the duty cycle was 0.5, the frequency was 5 Hz, the Ph was 2.5-3.5 and the temperature 50°C. After tin was plated to a thickness of 20 μm, the samples were transferred to a solution composed of 192 g/l potassium pyrophosphate, 71 g/l nickel chloride, 20 g/l stannous chloride and 20 g/l glycene at 60°C. Layers of NiSn of thicknesses between 50 and 250 nm were pulse plated at a peak current density of 600 A/m^2. The other pulse variables were the same as during tin plating. The samples were then returned to the tin-plating solution to deposit an additional 20 μm. Forty μm-thick single-layers of tin and of NiSn were also plated for comparison. The Ni/NiSn/Ni sandwiches were produced in the same way. The first and second nickel layers were plated in a standard Watts solution. The other conditions were the same as those already described for tin and NiSn plating.

The corrosion testing consisted of increasing the potential from -0.5 V vs a standard calomel electrode to + 1.5 V for the chromium deposits and to + 2 V for the sandwiches. The scanning rate was 1 mV/sec when chromium deposits were tested and 2 mV/sec for the sandwiches. The chromium deposits were tested in 5% hydrochloric and 5% and 10% sulfuric acids. The sandwiches were tested in 1% sulfuric acid. The corrosion currents were recorded. Some deposits were vacuum annealed before corrosion testing.

2

The internal stresses were measured during deposition using an electro-balance. The technique which has been previously (1) described in greater detail consists of insulating one side of a substrate strip which is gripped at one end and attached at the other end to the balance by means of a glass rod. When the uninsulated side is plated and a stress develops, the substrate tries to bend. Then the balance applies a force to prevent the bending. The applied force is recorded. The stresses are calculated from the dimensions of the substrate and the slope of the force-vs-thickness graphs.

The mechanical properties of the sandwiches were determined with the mini-tensile device which was described in the previous final report (2). Chemical analyses of the deposits were performed with energy-dispersive X-rays in a scan-ning electron microscope in which as-plated and corroded surfaces and metallo-graphically polished and etched cross sections were also examined. Some trans-mission electron microscopy was also performed. Knoop hardnesses were determined using a 100 g load. The plating solutions were chemically analyzed by titration.

The investigation of the attack of substrates involved weight-loss deter-minations in three different ways. Pieces of the steel and copper substrates were immersed in the various plating solutions for six hours. In the second way, pieces of the copper foil were immersed in the solutions with an applied current density (50-400 A/m^2) which was too low for chromium deposition. In these two methods the weight difference per unit area before and after immersion and the time yielded the attack rate. The third method involved weighing the substrate before plating, depositing chromium and weighing again. The deposit by itself was also weighed after dissolving the substrate. From these three weighings it was possible to calculate the weight loss of the substrate. However, as the time during which the substrate was attacked was not known, a rate could not be calculated. In some cases the dissolved substrate ions redeposited with the chromium to form alloy layers. The layers were chemically analyzed and their thicknesses determined by electron-microscopic examination of the cross sections.

RESULTS AND DISCUSSION

Structures

In order to produce various types of chromium multilayer deposits, it was first necessary to determine the conditions under which certain structures could be obtained. The various structures, i.e., body-centered-cubic and amorphous chromium and the hexagonal hydride could be deposited by varying the current density, the temperature and the concentration of the trivalent chromium ions. The concentration of trivalent ions in turn, depended on the concentrations of chromic and formic acids in the plating solutions. It was found that when no formic acid was present in the plating solution, which contained 250 g/l chromic acid, the deposits were bright and body-centered cubic with a <111> preferred orientation when plated between 45°C and 60°C and current densities of 1-10 KA/m^2. If the temperature of the plating solution was less than 45°C, the deposits were dull. When the formic-acid concentration exceeded 20 ml/l and the current density was greater than 4 KA/m^2 at ambient temperatures, the deposits were amorphous. When the current density was less than 4 KA/m^2, the deposits were crystalline. It was found by Auger electron spectroscopy that the carbon content in the amorphous deposits varied between 4% and 9%. The resulting

3

supersaturation probably caused the amorphous structure. Variations in the carbon content with thickness was the likely cause of the banded structure which was observed when a metallographically prepared cross section of the amorphous deposits was microscopically examined.

When the chromic-oxide concentration was 175 g/l and that of formic acid was only 0.5 ml/l, the hexagonal chromium hydride was produced at current densities less than 1 KA/m^2. At higher current densities, the chromium deposits were body-centered cubic. The hexagonal chromium hydride appeared to be randomly oriented. As the formic-acid concentration was increased, a <11.0> preferred orientation developed. Further increases in the amount of formic acid added to the solution resulted in the amorphous structure.

Corrosion

The results of the corrosion testing are illustrated in Figure 1. Typical graphs of potential vs current density in sulfuric acid and hydrochloric acids are shown. In sulfuric acid (dotted line) the corrosion rate, which is proportional to the current density, increases to Point A where passivation occurs. Point A is the critical current density. The corrosion rate then decreases and reaches a relatively constant value which is marked B. This current density is the one in the passive region. The sharp increase in the current density at still higher potentials occurs in the transpassive region where the film breaks down. In hydrochloric acid there is no decrease in the corrosion rate at the critical current at Point C. Therefore, the critical current density and that in the passive region are essentially the same.
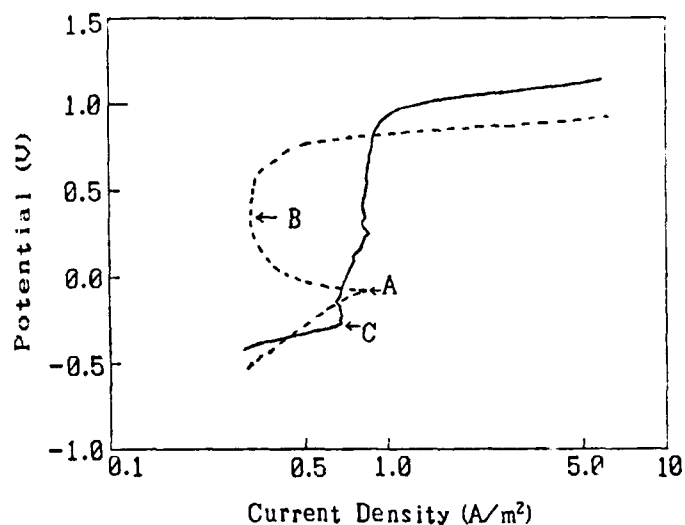

Fig. 1 Typical Voltammetry Graphs in Sulfuric (Dotted Curve) and Hydrochloric (Solid Curve) Acids

The critical and passive-region current densities for 2 μm-thick deposits in 5% sulfuric acid are listed in Table 1. It is evident from Table 1 that the deposits containing less than 0.4% Mo have higher critical and passive-region current densities than conventional chromium, i.e., they are less corrosion resistant. The deposits with higher molybdenum contents appear to be more corrosion resistant than chromium. The multilayer deposit has the lowest critical and passive-region current densities and is, therefore, the most corrosion resistant. Malinin and Falicheva (3) also found that the addition of potassium molybdate to the plating solution so that a Cr-Mo alloy formed, decreased the passivation current by a factor of 2.4. The corrosion of multilayer Cr-Mo deposits has not been previously studied.

The reason for the improvement in the corrosion resistance of the multilayer

4

Cr-Mo deposits ... pe ... due at least in part to the ... surface microstructure.

TABLE 1

Corrosion Data for Two Micrometer Thick Deposits in 5% Sulfuric Acid

Deposit	Critical Current Density (A/m²)	Passive Region C.D. (A/m²)
Chromium	3	2
Cr-0.1% Mo	11	1
Cr-0.3% Mo	5	1
Cr-0.4% Mo	2	1
Cr-0.8% Mo	2	1
Cr-1.4% Mo	2	1
Multilayer*	0.7	0.3

*Consisted of 250 nm alternate layers of chromium containing about 0.1 and 1.4% Mo, respectively.
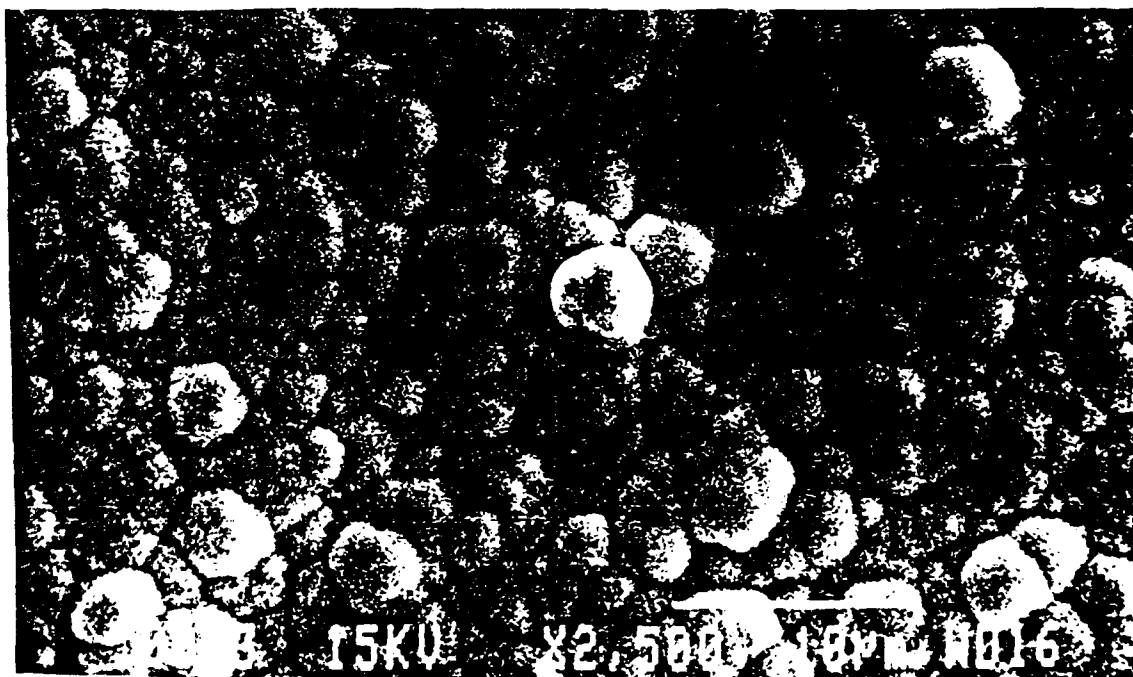

Fig. 2. Scanning Electron Micrograph of Surface of Multilayer Deposit

The surface structure is characterized by nodules as shown in Figure 2. The nodules are groups of very fine grains surrounded by a crevice. The crevices are more corrosion receptive as evidenced by the fact that they became deeper after exposure to the corrosive medium. The crevices are probably less corrosion resistant because of compositional differences which result in a slower growth rate. Hydride formation may be responsible for the crevices. As X-ray mapping showed a uniform molybdenum distribution, it is unlikely that variations in the alloy content caused the crevices. The decrease in the critical current density with increasing molybdenum content probably resulted from an increase in the nodule size, i.e., fewer crevices. If the corrosion current is concentrated in the crevices, the fewer there are, the higher is the current density there. Therefore, if there are few crevices, the critical current density is reached locally at a lower overall value. The deposition of multilayer deposits resulted in fewer and shallower crevices and thus in the lowest overall critical current density. The exposure of layers of different nobility to the corrosive medium at crevices, pits or other defects could result in a galvanic action. In this way, the critical current density would be reached at a lower applied potential. The overall current density would thus again be lower.

It appears that 2 μm is an optimum thickness for corrosion resistance for Cr-Mo deposits. Deposits thinner than 2 μm did not exhibit any passivity. Pits which had reached the steel substrate were observed. Apparently the deposit under the crevices was too thin or nonexistent. Thus before reaching the critical current density, the steel became exposed to the acid. Five μm-thick deposits exhibited some fine cracks which followed the crevices surrounding the nodules. The cracks were due to the high stresses which are characteristic of many chromium deposits and which will be subsequently discussed. The critical and passive-region current densities for 5 μm-thick deposits are listed in Table 2.

TABLE 2

Corrosion Data for Five-Micrometer-Thick Deposits in 5% H_2SO_4

Deposit and Heat Treatment	Critical Current Density (A/m^2)	Passive Region C.D. (A/m^2)
Cr-0.3% Mo As-plated	11	0.8
Cr-1.4% Mo As-plated	17	0.7
Cr-0.3% Mo, 10 hrs at 70°C	4	0.3
Cr-1.4% Mo, 10 hrs at 70°C	14	0.4
Cr-0.3% Mo, 2 hrs at 120°C	1	0.3
Cr-1.4% Mo, 2 hrs at 120°C	4	0.3

The higher critical current densities of the 5 μm-thick deposits were probably due to the fine cracks. In the transpassive region, wide cracks developed. The 2 μm-thick deposits showed no cracks after exposure in the transpassive region. Apparently, the stresses had not reached the magnitudes for cracking in the 2 μm-thick deposits. The high stresses have been attributed to hydrogen (4). To assess the effect of hydrogen, the 5 μm-thick deposits were vacuum annealed. The

corrosion current densities of the annealed deposits are also listed in Table 2. Evidently, annealing to drive off hydrogen resulted in a lowering of the critical and passive-region current densities. Possibly, the crevices became more corrosion resistant because of a lower hydrogen content and internal stress. However, as the annealed deposits still cracked during exposure in the transpassive region, there must have been other causes of stress.

The results of corrosion testing in HCl of several 3 μm-thick single and multilayer deposits are listed in Table 3. Except for the chromium listed first and the Cr-Mo deposits, all others were plated in the solution containing formic acid which causes some ions to be in the trivalent state. As seen from Figure 1, the passive-region current density increased somewhat with increasing potential in hydrochloric acid. The values in Table 3 are averages of at least three measurements.

TABLE 3

Corrosion Data for Three-Micrometer-Thick Deposits in 5% HCl

Deposit	Cri ical Current Density (A/m^2)	Passive Region C.D. (A/m^2)
Cr (Hexavalent)	No passivity	
Cr-2% Mo	1	2
Multilayer Cr-Mo*	0.3	0.4
Crystalline Cr#	8	14
Amorphous Cr#**	0.3	0.3
Crystalline-Amorphous Multilayer#	0.3	0.3
Cr Hydride#	2	5
Crystalline-Hydride Multilayer#	2	5

*Cr and Cr-2% Mo layers. #Plated in solution containing 40 g/l formic acid. **Banded structure. Individual layers in multilayer deposits were 250 nm thick.

It can be seen from Table 3 that the multilayer Cr-Mo and the crystalline (bcc)-amorphous deposits as well as the one with the banded structure, which can be considered a naturally occurring multilayer one, show better corrosion resistance than the others. It appears that crystalline layers had no significant effect on corrosion resistance because the amorphous deposit was already a multilayer one. Crystalline (bcc) chromium whether deposited in a solution containing only hexavalent or some trivalent ions due to the addition of formic acid, shows poor corrosion resistance in hydrochloric acid. Apparently having crystalline chromium alternate with the hydride, did not improve the corrosion resistance.

The reasons for the better corrosion resistance of Cr-Mo multilayer deposits have already been discussed. The amorphous deposits probably had better corrosion resistance because defects did not extend throughout the thickness due to the banded structure. The probable reason why the corrosion current did not decrease after the critical current density was that the mechanism was one of pit formation and healing. This mechanism would be prevalent at the onset of passivity and throughout the passive region.

The results of corrosion testing in 10% hydrochloric acid are shown in Table 4. The deposits are the same as those listed in Table 3.

TABLE 4

Corrosion Data for Three-Micrometer-Thick Deposits in 10% HCl

Deposit	Critical Current Density (A/m^2)	Passive Region C.D. (A/m^2)
Cr (Hexavalent)	No passivity	
Cr-2% Mo	No passivity	
Multilayer Cr-Mo	No passivity	
Amorphous Cr	0.4	0.5
Crystalline-Amorphous Multilayer	0.4	0.5
Cr Hydride	3.5	7.0
Crystalline-Hydride Multilayer	3.7	7.0

It is seen from Table 4 that the amorphous chromium and the hydride withstand the more concentrated hydrochloric acid solution and that there appears to be no advantage in having crystalline chromium present as one of the alternate layers.

Sandwiching a 150 μm-thick layer of NiSn between nickel prevented pits from reaching the substrate. There were fewer but wider pits when the sandwiches were tested in 1% sulfuric acid. Apparently when a pit reached the intermetallic phase, which was cathodic to nickel, it spread sideways rather than penetrating to the substrate. The interruption of nickel plating to deposit NiSn probably also resulted in fewer defects which developed into pits. However, the NiSn layer raised the critical current density. The critical and passive-region current densities of Watts nickel in 1% sulfuric acid were about 10 A/m^2. When a 150 nm-thick layer of NiSn, which as will be discussed later resulted in the optimum mechanical properties, was sandwiched between 20 μm-thick nickel, the critical current density increased to 50 A/m^2. The passive-region current density did not change. Thus the corrosion rate was not improved. Tin with and without a NiSn layer did not passivate in 1 sulfuric acid. When a pit reached

the NiSn layer, corrosion was accelerated so that the top tin layer rapidly disappeared.

Substrate Attack

The chrome-plating solutions were found to attack the low-carbon steel, copper and nickel substrates. When the substrates were immersed in the solution without an applied current, the weight-loss rates were 70 nm/hr, 90 nm/hr and 60 nm/hr for steel, copper and nickel, respectively, in the solution containing only chromic oxide and sulfuric acid. In the chrome-plating solution which contained 40 ml/l formic acid which resulted in the presence of 20 g/l trivalent chromium ions, the steel, copper and nickel substrates dissolved at rates of 100, 80 and 70 nm/hr, respectively. When a small cathodic current which was insufficient to result in any chromium deposition was applied, the copper substrate dissolved at a rate of about 5000 nm/hr in both solutions. When the current density of 4 KA/m^2, which resulted in chromium deposition, was applied, a substrate attack rate could not be determined. It was found that copper substrates lost 1.5 mg/cm^2 in the solution containing no formic acid and 4.3 mg/cm^2 in the one with 40 ml/l formic acid. When only 20 ml/l formic acid had been added to the plating solution, only 15 g/l trivalent chromium ions were found to be present. Copper substrates then lost 3.2 mg/cm^2.

The increased attack rate with increasing cathodic current at first seems anomalous. A cathodic potential should prevent corrosive attack. However, the cathodic potential actually reduced the oxide which was the source of passivity. Similar phenomena have been observed by others (5,6).

When chromium was plated in the solution containing 20 ml/l trivalent chromium ions, the metal ions of the substrate which had dissolved, redeposited to form alloy layers. No alloy-layer formation was observed when only 15 g/l trivalent chromium ions were present in the plating solution. The alloy layer which had formed on a copper substrate is shown in Figure 3. The alloy layer on copper substrates contained between 20% and 35% Cu and was about 10 μm thick. By means of selected-area electron diffraction it was determined that the alloy layer consisted of two phases. Diffraction spots belonging to copper and to chromium could be indexed. As chromium and copper are essentially insoluble on each other, a two-phase structure would be expected. The two phases existed as alternate layers. The initial Cr-Cu alloy layer was mostly amorphous as indicated by one broad ring in the electron diffraction pattern. It was amorphous probably because it was a highly supersaturated solid solution. However, there were a few distinct spots also present. Possibly the very first layer grew epitaxially on the substrate.

The alloy layer which formed on the low-carbon steel substrate contained between 4% and 17% Fe. It was about 5 μm thick and was a single-phase solid solution. On nickel substrates the alloy layer had the same thickness and contained between 20% and 30% Ni. It was also a single phase. The reason for the one-phase structures is undoubtedly the higher solid solubility of chromium in iron and nickel compared to copper.

It was determined that the metal ions which codeposited to form the alloy layers were the ones resulting from the substrate attack. Several results showed
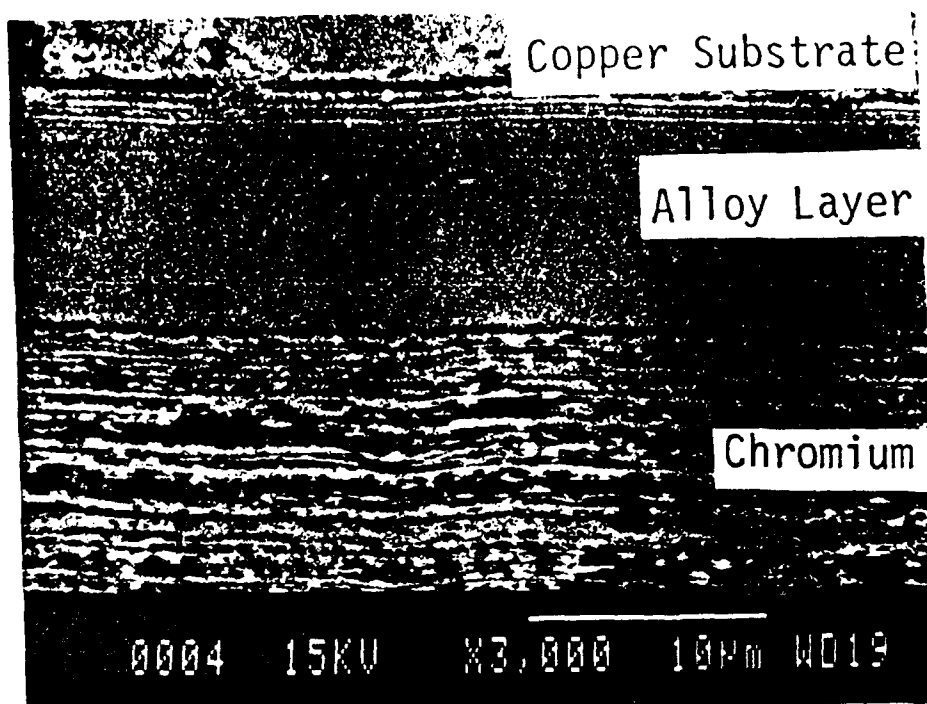
9

Fig. 3   Scanning Electron Micrograph of Cross Section Showing Copper Substrate, Alloy Layer and Chromium Deposit

it to be so. When the substrates were first covered with chromium plated in the solution which did not contain formic acid and in which alloy layers did not form, none formed subsequently. Evidently the first chromium deposit which had covered the substrate prevented attack in the solution in which alloy layers could have formed. Therefore no substrate-metal ions were present in the solution when the substrate was not attacked. Alloy layers would have formed in this solution if the substrate had been attacked. Even when copper sulfate was added to the solution, no alloy layers formed as long as previously deposited chromium layers protected the substrate from attack. It was also apparent that metal ions which codeposited must have originated from the substrate attack and remained in the vicinity of the substrate. The weight of copper in a 5 μm-thick alloy layer containing 35% Cu is 1.4 mg/cm^2 which compares to a weight loss of 4.3 mg/cm^2. Thus there was sufficient copper dissolved to form the alloy layer after redeposition as long as most of the ions remained in the vicinity of the substrate.

The mechanisms involved in alloy-layer formation are undoubtedly complicated. It is evident that a minimum concentration of trivalent chromium ions is required for the alloys to form. It appears that the redeposition of copper involves the oxidation of trivalent chromium ions to hexavalent ones. Mitskus and Sklenikaite (7) found that the dissolution of copper involved the reduction of hexavalent to trivalent chromium. The reverse reaction is therefore also to be expected. Alloy-layer formation, therefore, appears to depend on substrates being attacked and sufficient trivalent ions being present to permit redeposition. The deposition potentials were found not to have been changed sufficiently by the trivalent ions so as to make deposition possible.

There was an apparent effect of either the Cr-Fe alloy layers or the formic-acid concentration in the plating solution on the corrosion resistance. Three μm-thick chromium deposits plated in a solution containing only 20 ml/l formic acid in which no alloy layer formed, had critical and passive-region current densities of 2 KA/m^2 in 5% HCl. When the solution contained 40 ml/l formic acid so that the deposits contained alloy layers, the current densities were 0.3 KA/m^2. In the transpassive region, only pitting was observed in the deposits containing alloy layers. Deposits without alloy layers also exhibited cracking due to their higher internal stresses which will be subsequently discussed.

Internal Stresses

Internal stresses can significantly affect the corrosion resistance. They can cause the deposit to crack and expose the substrate. Even in the absence of cracking, internal stress can reduce the corrosion resistance. In order to understand the phenomena of internal stresses, it is preferable to determine their variation with deposit thickness rather than obtaining an average value. The instantaneous stress, which can be determined from variation with time of the force exerted by the electrobalance to prevent bending, is that remaining in each layer of the deposit. The force exerted in an infinitesimal time interval is due to the stress in the layer being deposited and relaxation beneath it. As no relaxation was observed after plating ceased, it can be assumed that this phenomenon takes place only in the layer deposited in the preceding time interval. It can further be assumed that the relaxation does not change significantly over one time interval. Thus, the force is due to the stress resulting from the deposition of the layer and its relaxation. Thus the instantaneous stress is the one remaining in the layer.

The shape of all the graphs of instantaneous stress vs deposit thickness were similar. Typical graphs for chromium deposits from a conventional (hexavalent) solution on steel and copper substrates are shown in Figure 4. There is an initial tensile stress which increases to a maximum value followed by a decrease. The stress may become compressive as is the case on the steel substrate seen in Figure 4. The stress then oscillates. The initial tensile stress may have several causes. It has been proposed (7) that hydrogen diffusing out of the deposit results in a contraction which results in a tensile stress when restrained by the substrate. If hydrogen diffuses into the substrate and expands it, an additional tensile stress develops in the deposit. The expansion of the substrate could be the reason why the tensile stress in some instances was greater in a chromium deposit on steel than in one on copper as hydrogen can readily diffuse into the former but not the latter. Another cause of the initial tensile stress could be the coalescence of crystallites before the spaces between them have been completely filled. Surface tension would tend to pull the crystallites together resulting in a contraction of the initial layer of the deposit. The stress decrease can also be due to several factors. If hydrogen no longer diffuses out of the deposit, the stress would decrease. New crystallites can develop between existing ones and cause an expansion. It has been proposed (8) that the deposit cracks due to a large tensile stress which would then be relieved. Deposition into the cracks would expand the deposit and could result in a compressive stress. Scanning-electron-microscopic examinations of the surface of deposits having thicknesses in the range between the maxima and the first minima did not reveal any crack formation. It is possible that the cracks

11

were too fine to be resolved. Transmission electron microscopy could not be used because dissolving the substrate was found to introduce fracture. The oscillations which followed the first maximum was found to be due to repeated fracture of the deposit and deposition into the cracks.

When alloy layers formed, the stress maxima were lower. On a steel substrate the maximum stress value was 280 MPa compared to 1070 MPa seen in Figure 4. On copper substrates the maximum value was 250 MPa versus 1230 MPa in Figure 4. When an alloy layer was present, the minimum generally occurred at a greater deposit thickness. When deposition took place in a solution with a formic-acid content of only 0.5 ml/l which was too low for alloy-layer formation, the stress maxima were larger being about 700 MPa on copper and 1020 MPa on steel substrates.
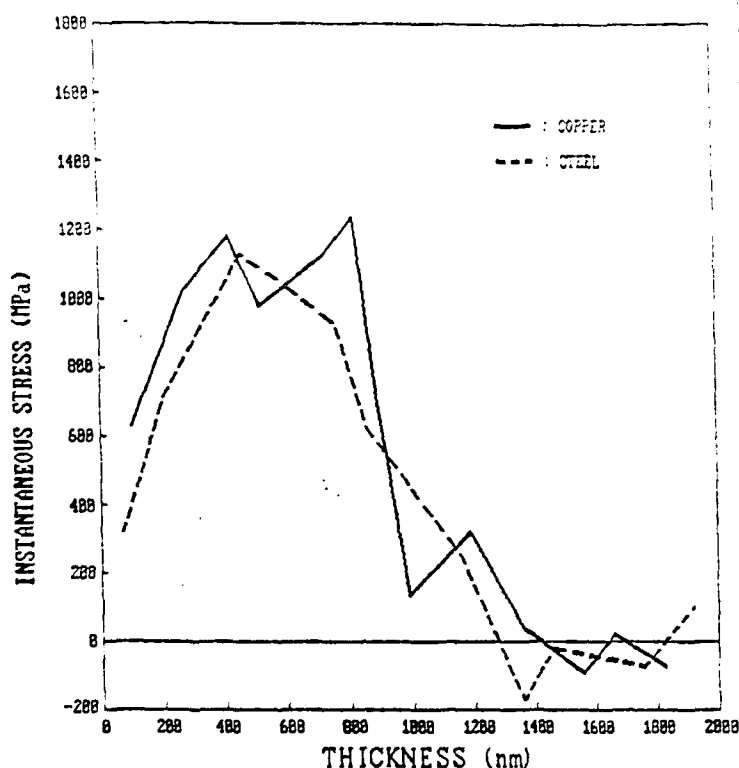
Fig. 4 Instantaneous Stress vs Deposit Thickness

It was not possible to separate the effects due to the alloy layers and the formic-acid concentration. When 500 nm of chromium were deposited first in the solution containing no formic acid and plating was continued in a second solution in which alloy layers would have formed if the bare substrate had been inserted, the stress maximum occurred only in the first deposit. In the second solution, only stress oscillations were observed. A probable reason for the lower stress in the alloy layer was its relatively large grain size. The coalescence stresses would therefore be smaller. The codeposition of the substrate ions to form the alloy layers could also have hindered the diffusion of hydrogen out of the deposit and thereby reduced this cause of tensile stresses.

When the current density in the low-concentration, formic-acid solution was only 1 KA/m^2 so that the hexagonal hydride formed, the stresses were small. The maximum instantaneous stress on a copper substrate was 300 MPa and 280 MPa on steel. The reasons for the lower stresses in the hydride deposit are probably that hydrogen is more stable and therefore less diffused out of the deposit and again its relatively large grain size.

12

The stress maxima in the Cr-Mo deposits were the largest. The deposit containing about 1.4% Mo on steel had a maximum stress of 1560 MPa and 1630 MPa on copper. The maxima also occurred at a thickness less than 1 μm, which is smaller than that in the other deposits. One probable reason for the high maximum stresses is the very small grain size. The observation that the thickness at which the stress started to decrease was smaller the higher the value at the maximum, would indicate that fracture was involved. Even though no cracks were observed, their formation to relieve the stress would be expected to occur sooner when the maximum was larger.

Tribology

The hardnesses and coefficients of static and dynamic fraction are listed in Table 5. The deposits are the same as those listed in Table 3 except that the total thickness was greater for the hardness measurements. It is seen that the

TABLE 5

Hardness and Friction Coefficients of Chromium Deposits

Deposit	Knoop Hardness Number*	Static Friction Coefficient**	Dynamic Friction Coefficient**
Cr (Hexavalent)	980	0.25	0.19
Cr-2% Mo	890	0.28	0.19
Cr-Mo Multilayer	680	0.15	0.18
Crystalline Cr	680	0.13	0.18
Amorphous Cr	650	0.12	0.12
Crystalline-Amorphous Multilayer	825	0.12	0.12
Cr Hydride	830	0.18	0.17
Crystalline-Hydride Multilayer	780	0.16	0.17

*100g load; **2 Kg load

conventional chromium deposit was the hardest. The multilayer deposit consisting of alternate crystalline and amorphous layers is harder than the single layers of which it was composed. However, the other two multilayer deposits are not as hard as at least one of its constituent single layers by itself. Thus no generalization about the hardness of multilayer chromium deposits can be made. There also appears to be no direct relationship between hardness and the friction coefficients. The friction coefficients of the deposits plated in the solution to which formic acid had been added and which consequently contained trivalent chromium ions, are lower than those of conventional chromium. As the multilayer deposits did not exhibit significantly lower friction coefficients, it can be

concluded that the bonding between the individual layers was sufficiently strong so that they did not slide over each other.

Several attempts were made to obtain quantitative wear data. The tracks made when a hardened steel ball was dragged over the deposit surfaces to determine the dynamic coefficient of friction, were very shallow. When a sensitive profilometer was used to determine the heights and widths of the wear tracks, the noise was of the same order of magnitude as the measurements. Attempts to determine the dimensions of the wear tracks using a scanning electron microscope also did not yield accurate quantitative data. From the appearance of the tracks as observed in the scanning microscope, it seemed that the wear of the multilayer deposits was not significantly different from that of the single-layer ones. A probable reason for this lack of a difference was the shallowness of the tracks. The tracks may have been confined to the top layer.

Mechanical Properties of Sandwiches

The effect on the mechanical properties of sandwiching a layer of the intermetallic phase NiSn between layers of nickel or tin is shown in Table 6.

TABLE 6

Mechanical Properties of Ni/NiSn/Ni and Sn/NiSn/Sn Composites

NiSn Thickness (nm)	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)
Ni/NiSn/Ni			
0	285	445	3
50	370	600	3
100	370	615	3
150	375	615	3
200	355	590	3
240	395	645	3
350	370	625	3
400	375	620	3
Sn/NiSn/Sn			
0	17	18	23
50	20	24	6
100	21	25	6
150	23	26	6
200	24	27	5
250	27	31	3

It can be deduced from Table 6 that depositing NiSn between layers of nickel increased the yield and tensile strength without adversely affecting the ductility. The optimum thickness of the intermetallic phase appears to be 150 nm. For this reason, as may be recalled, composites with a 150 nm-thick layer were the ones which were corrosion tested. The main disadvantage of producing

14

these composites is the necessity of moving the deposit from the solution in which nickel was deposited into another one to plate the intermetallic phase and then returning it. Therefore only one layer of NiSn was deposited.

Sandwiching NiSn between tin layers increased the strength but adversely affected the ductility. As these composites also exhibited poor corrosion resistance, they are not deemed to be practical.

CONCLUSIONS

1. The corrosion resistance in sulfuric acid can be improved by alloying chromium with molybdenum and further by depositing alternate layers of different compositions as long as the thickness does not exceed values at which cracking occurs.

2. Crystalline-amorphous multilayer deposits and those having a banded structure have superior corrosion resistance especially in hydrochloric acid.

3. Chrome-plating solutions attack substrates. When the trivalent-ion concentration reaches a critical value, alloy layers form. The alloying elements originate from the substrate attack.

4. Graphs of instantaneous internal stress vs deposit thickness show an initial tensile stress maximum and oscillations after the decrease. Chromium-molybdenum deposits show the largest stress maximum. In alloy layers, the stress maximum is smaller than in conventional chromium and occurs at greater thicknesses.

5. No generalizations could be made by comparing the hardnesses and coefficients of friction of single and multilayer deposits.

6. The deposition of an intermetallic phase, NiSn between layers of nickel increased the yield and tensile strength without adversely affecting the ductility. The layer of NiSn also prevented corrosion pitting from reaching a steel substrate.

REFERENCES

1. H. Feigenbaum and R. Weil, **J. Electrochem. Soc., 126** (1979) 2085.

2. R. Weil and C. C. Nee, **Final Report for ARO Grant DAAG-27-80-C-0056**. Sept. 1, 1983.

3. V. F. Malinin and A.I. Falicheva, **Zashchita Metallov, 18** (1982) 954.

4. B. V. Adzhiev and Z. A. Soloveva, **ibid, 15** (1979) 481.

5. L. S. Audzionene, A. Yu. Mitskene and M. A. Mitkus, **Electrodeposition of Metals, Proc. 10th Lithuan. Conf. Electrochem.**, Yu. Yu. Matulis, Ed., Lithuan. Acad. Sci. (1968) 69, NBS Eng. Transl.

6. B. Bulotaite, V. Skominas and Yu. Bubyalis, **ibid.**, 73.

7. M. A. Mitskus and D. I. Sklenikaite, **ibid.**, 65.

8. W. H. Cleghorn and J. West, **Trans. Inst. Met. Finish,** **44** (1966) 105.

ACTIVITIES

Two Ph.D. degrees were awarded to persons supported by this study. W. Kim was awarded the doctorate in May 1988 with a thesis entitled: "Pulse-Plating Effects on the Properties of Nickel and Ni-Mo Electrodeposits." C. Sheu received the degree in May 1990 with a thesis entitled: "Structure and Properties of Multilayer Chromium Deposits."

The following papers were published in refereed technical publications based on work totally or partially supported by the Army Research Office:

1. I. Kim and R. Weil, "Tension Testing of Very Thin Electrodeposits," **Testing and Metallic and Inorganic Coatings, ASTM STP, 947**, W. B. Harding and G. A. DiBari, Eds., American Society for Testing and Materials, Philadelphia, PA (1987) 11.

2. W. Kim and R. Weil, "Property Enhancement of Nickel Electrodeposits by Anodic Current Pulses," **Surface and Coatings Technology,** **31** (1987) 143.

3. C. C. Nee and R. Weil, "Pulsed Electrodeposition of Ni-Mo Alloy," J. **Electrochem. Soc.,** **135** (1988) 1100.

4. R. Weil, C. C. Nee and J. W. Chang, "Pulsed Electrodeposition of Layered Brass Structures," **Metallurgical Trans.,** **19A** (1988) 1569.

5. W. Kim and R. Weil, "Pulse Plating Effects in Nickel Electrodeposition," **Surface and Coatings Technology,** **38** (1989) 289.

6. I. Kim and R. Weil, "The Mechanical Properties of Monocrystalline Electrodeposits, **Thin Solid Films,** **169** (1989) 35.

7. C. Sheu and R. Weil, "Multilayer Electrodeposited Coatings for Corrosion Protection," **Corrosion 90 (Proc. National Soc. Corrosion Eng. Ann. Meeting (1990) Paper 449**.

8. C. Sheu and R. Weil, "Substrate Interaction Effects on the Structure of Chromium Electrodeposits," **J. Electrochem. Soc.,** **137** (1990) 2052.

A paper entitled "Corrosion Resistance of Multilayer Electrodeposited Coatings" by C. Sheu and R. Weil was presented at the Tri-Service Corrosion Conference in Atlantic City, NJ in Nov. 1989.

The above Paper No. 7 was invited and presented at the National Meeting of NACE in Las Vegas in April 1990.

A paper entitled "Multilayer Electrodeposited Coatings" by C. Sheu and R. Weil was presented at The Metallurgical Soc. Regional Meeting on Composites in Morristown, NJ in June 1990.

United States Patent 4,869,971 entitled "Multilayer Pulsed-Current Electrodeposition Process" was issued on September 26, 1989 to C. C. Nee and R. Weil.